NITROSAMINES IN TAP WATER AFTER CONCENTRATION BY A CARBONACEOUS ADSORBENT

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Abstract—Ambersorb XE-340 carbonaceous adsorbent removed trace levels of volatile nitrosamines (NAs) that were added to the influent water. Recovery of seven added NAs was between 58–99% as determined by a gas-liquid chromatograph interfaced with a Thermal Energy Analyzer (GLC-TEA). When municipal (tap) water (10–42 l.) was passed through the Ambersorb XE-340 column, N-nitroso-dimethylamine (NDMA; 0.003–0.006 $\mu g\ l^{-1}$) and -morpholine (NMOR; 0.006–0.018 $\mu g\ l^{-1}$) were the principal NAs found. All of the NDMA and 18 of 20 NMOR samples were confirmed by high resolution mass spectrometry. Secondary amines added to tap water at levels of 1 $mg\ l^{-1}$ and 10 $\mu g\ l^{-1}$ formed apparent NAs, suggesting a possible component(s) in the water that caused NA formation. Low levels of volatile NAs were detected by GLC-TEA in commercial, pure, adsorbents (activated carbon). NAs were confirmed by high resolution mass spectrometry except where concentrations were too low. In the latter case, the apparent NAs were found to be photolabile when subjected to u.v. light (365 nm) and were reanalyzed by GLC-TEA thus providing additional evidence that the TEA responsive compounds were NAs.

INTRODUCTION

Nitrosamines (NAs) and their precursors, nitrite and amines, are ubiquitous in the environment. Nitrite can be formed by the nitrification of ammonia or denitrification of nitrate by microorganisms. Decomposition of organic materials of plant and animal origin, industrial (chemical) discharge, and pesticide preparations are primary sources of environmental amines. With the simultaneous presence of nitrite and amines in the water supply, the potential exists for the formation of NAs in drinking water.

To our knowledge no one has observed NAs in drinking water to date. The available data suggest that if NAs are present in drinking water, they will be at levels considerably below 1 $\mu g\ l^{-1}$. There is some information on the occurrence of Thermal Energy Analyzer (TEA) responsive compounds in drinking water. The selectivity of the TEA to NAs is based on the detection of chemiluminescent emission resulting from the decay to the ground state of excited nitrogen dioxide formed by the reaction of nitric oxide with ozone. Therefore, any compound capable of liberating NO under the pyrolytic conditions of the TEA will give a positive response. At a detection level of greater than 0.002 $\mu g\ l^{-1}$ no volatile TEA responsive peaks were observed in drinking water from New Orleans, LA, and Boston, MA, areas by Fine *et al.* (1975). Although a high performance liquid chromatograph (HPLC) interfaced with a TEA revealed at least 24 TEA responsive peaks in New Orleans area drinking water, none was identified positively as NA. Water from Cincinnati, OH, Washington, DC, and Philadelphia, PA, obtained after treatment, gave three TEA responsive peaks when analyzed by HPLC-TEA by Fan *et al.* (1978), but again, none was thought to be NA; one peak was identified as ethyleneglycol dinitrate.

Although NAs have not been found in drinking water, they have been found in natural waters. Fine and Rounbehler (1976) detected N-nitrosodimethylamine (NDMA; 0.08–2.7 $\mu g\ l^{-1}$), possibly of industrial origin, in the Curtis Bay, Baltimore, MD. NAs have been detected in deionized water, with reported levels of: NDMA 0.01 $\mu g\ l^{-1}$ (Gough *et al.*, 1977), 0.03–0.34 $\mu g\ l^{-1}$ (Fiddler *et al.*, 1977), and 0.25 $\mu g\ l^{-1}$ and lower concentrations (Cohen & Backman, 1978); and N-nitrosodiethylamine (NDEA) 0.33 and 0.83 $\mu g\ l^{-1}$ (Fiddler *et al.*, 1977).

The primary purpose of our investigation was to determine the levels of volatile NAs that may be present in the municipal (tap) water supply at the Eastern Regional Research Center. The water company that supplies the tap water to the Center obtains the natural water from several sources, from both surface and ground water.

EXPERIMENTAL

All of the solvents used in these experiments were tested and shown to be free of volatile NAs by gas-liquid chromatography GLC-TEA.

Determination of the presence of NAs in pure adsorbents

Approximately 100 g of Ambersorb XE-340 (Rohm & Haas, Philadelphia, PA), Filtrasorb 300 and 400 (Calgon Corp., Pittsburgh, PA), Westvaco Nuchar WVW, 8 × 30 and 12 × 40 mesh and WVG, 12 × 40 mesh (Westvaco Corp., Covington, VA), or ICI Hydro-Darco, 10 × 30

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mesh (ICI, Wilmington, DE) was placed in a 500 ml Erlenmeyer flask, and 200 ml dichloromethane (DCM; Burdick & Jackson, Muskegan, MI) was slowly added. The DCM-adsorbent mixture was allowed to stand for at least 1 h, then was transferred to a 31 × 390 mm chromatographic column containing a glass wool plug and eluted with 500 ml DCM over a 2 h period. The DCM was dried over anhydrous Na_2SO_4 and concentrated in a Kuderna–Danish evaporator to 1.0 ml on a steam bath and analyzed for NAs.

Hydration of Ambersorb XE-340 prior to isolation of NAs

In order to wet the Ambersorb XE-340 carbonaceous adsorbent, the sample was first covered for 1 h with methanol (that was purified by the method of Erickson & Dunkley, 1964). Then 90 ml wet volume of adsorbent was packed in a 21 × 340 mm chromatographic column and washed with 10–20 bed vol of distilled water over a period of 1–2 h prior to use.

Isolation of NAs from tap water with the Ambersorb XE-340 accumulator

Ambersorb XE-340 was packed in a 26 × 260 mm copper pipe equipped with copper fittings on both ends. One fitting was connected to the faucet and the other to a valve to control the flow rate. Water was sampled for 8.5–11.75 h for NAs, twice a week, from 23 May to 14 June 1978, and for 64–95 h, twice a week, from 28 July to 31 August 1978. The 23 May to 14 June 1978 water samples were analyzed also for nitrite and nitrate; no other analysis was carried out on the water. When the experiment was completed, the pipe was disconnected from the faucet, the adsorbent was transferred into a 21 × 340 chromatographic column, and the column was left standing overnight.

Elution of NAs from Ambersorb XE-340 accumulator

Water was drained from the column at ambient pressure, 60 ml of methanol was added, and the column was allowed to stand for *c.* 30 min; then an additional 40 ml methanol was added to remove the water from the column. The effluent was collected in an Erlenmeyer flask containing 200 ml distilled water. DCM (700 ml) was next passed through the column over a period of *c.* 6 h. The methanol–water mixture was extracted with the first 300 ml, the next 200 ml, and the last 200 ml of DCM eluted. The first 500 ml DCM contained more than 92% of the NAs. The DCM extracts were combined and concentrated as described previously.

Regeneration of Ambersorb XE-340

The adsorbent was air dried or placed on the steam bath to remove residual DCM, then dried overnight in a 110°C oven. The dried adsorbent was placed in a chromatographic column containing DCM and eluted with 400 ml DCM. When the concentrate from the last 200 ml of eluent was found to be free of N-nitroso responsive peaks as determined by GLC-TEA, the Ambersorb XE-340 was again air dried or placed on the steam bath to remove DCM and heated in the 110°C oven overnight prior to reuse.

Recovery of NAs by Ambersorb XE-340

To determine the efficiency of NA removal from water by Ambersorb XE-340, 3 l. of distilled water with and without added 150 ng each of NDMA, NDEA, N-nitrosomethylethylamine (NMEA), N-nitrosopiperidine (NPIP), N-nitrosopyrrolidine (NPYR), N-nitrosomorpholine (NMOR) and N-nitrosohexamethylenimine (NHMI) was passed through Ambersorb XE-340 packed in chromatographic columns over a period of 2.5–4 h. A similar experiment was carried out with 30 l. of tap water, with and without added 150 ng ($0.005\ \mu g\ l.^{-1}$) of the above 7 NA standards. These solutions were passed through Ambersorb XE-340 chromatographic columns over a period of 3 days (10 l. per day at a flow rate of $1\ l.\ h^{-1}$).

Addition of amines and $NaNO_2$ to tap water prior to passage through Ambersorb XE-340

Dimethylamine (DMA) and diethylamine (DEA) were purified by recrystallizing their hydrochloride derivatives; morpholine (MOR; Fischer Scientific Company, Fair Lawn, NJ) was used without further purification. Stock solutions of $NaNO_2$ and amines ($1\ g\ l^{-1}$) were prepared and were subsequently added to tap water ($3 \times 3\ ml\ 3\ l^{-1}$) and $1 \times 1\ ml\ l^{-1}$ for a total of 10 l. of $1\ mg\ l^{-1}$ solutions) prior to passage through the Ambersorb XE-340 column. The NAs were eluted from the Ambersorb XE-340 column as described previously. To determine the NAs content, 10 ml each of $NaNO_2$ and amine stock solutions was diluted with 90 ml distilled water, and each extracted with 3 × 100 ml DCM. NAs were not detected in the $NaNO_2$ solution. The amine solution did not contain NDMA, but did contain small amounts of NDEA (2 ng) and NMOR (23 ng). These concentrations of NAs would have contributed only $0.0002\ \mu g\ l^{-1}$ for NDEA and $0.0023\ \mu g\ l^{-1}$ for NMOR (Table 4), and therefore had no effect on the experimental results.

Addition of amines to tap water prior to extraction with DCM

One $mg\ l^{-1}$ or $10\ \mu g\ l^{-1}$ each of DMA, DEA and MOR was added to tap water with and without 105 ng NHMI internal standard per l. The mixture was allowed to stand for 3 h, then 500 ml was extracted with 3 × 150 ml DCM. Na_2SO_3 (50 or $100\ mg\ l^{-1}$) was added to the remaining 500 ml, and the mixture was allowed to stand for 30 min prior to extraction with DCM. In a separate experiment $50\ mg\ l^{-1}$ Na_2SO_3 was added to tap water containing 105 ng NHMI l^{-1}, allowed to stand 30 min and $1\ mg\ l^{-1}$ of the amines was added. The mixture was allowed to stand an additional 2.5 h prior to extraction with DCM. The DCM extracts were concentrated as described previously.

Addition of sulfamic acid, piperidine, and Na_2SO_3 prior to passage through Ambersorb XE-340

The following solutions were prepared in 9 × 3 l. batches (a total of 27 l.) and passed through the Ambersorb XE-340 column at the rate of $1\ l.\ h^{-1}$, $9\ l.\ day^{-1}$ over a 3-day period.

1. To 3 l. samples of tap water containing 10 ng NHMI were added: (a) sufficient piperidine (purified by preparation of the hydrochloride derivative) solution to obtain a final amine concentration of $100\ \mu g\ l^{-1}$; and (b) a mixture of 30 ml of a 10% sulfamic acid (Pfaltz & Bauer, Inc., Stamford, CT) and piperidine solutions to yield final concentrations of $1000\ mg\ l^{-1}$ and $100\ \mu g\ l^{-1}$, respectively.

2. To 6 l. of tap water containing 20 ng NHMI was added 6 ml of 10% Na_2SO_3 solution equivalent to $100\ mg\ l^{-1}$ Na_2SO_3. The mixture was allowed to stand for 30 min, then divided into two 3 l. portions. To one was added a mixture of 30 ml sulfamic acid solution and a piperidine solution to yield a final concentration of $100\ \mu g\ l^{-1}$ with respect to the amine. To the other, only piperidine was added (final concentration, $100\ \mu g\ l^{-1}$). The mixtures from Exp. 1 and 2 were allowed to stand for 1 h prior to passage through the Ambersorb XE-340 column.

3. Distilled water (6 l.) containing 20 ng NHMI was divided into two 3 l. portions. To one portion was added 3 ml 10% Na_2SO_3, 30 ml sulfamic acid and piperidine (100 ppb final concentration) solutions. This mixture and the remaining 3 l. portion were passed through the Ambersorb XE-340 column.

The piperidine stock solution used, which varied from 81 to $237\ mg\ l^{-1}$, and the 10% sulfamic acid solution were prepared daily.

Analysis for nitrate and nitrite

Nitrate present in tap water was reduced to nitrite with metallic Cd by the method of Kamm *et al.* (1965), and nitrite was determined by the Griess colorimetric method (Fiddler, 1977). Low levels of nitrite present in tap water also were determined by differential pulse polarography (Chang *et al.*, 1977) by use of a Polarographic Analyzer (Model 174, Princeton Applied Research, Princeton, NJ). This procedure involved the formation and detection of N-nitrosodiphenylamine.

General method for the analysis of NAs

Samples (7–8 μl) from 1.0 ml concentrates of DCM extracts were injected into a Varian-Aerograph gas-liquid chromatograph (GLC; Model 2700, Varian Assoc., Palo Alto, CA) interfaced with a Thermal Energy Analyzer (TEA; Model 502, Thermo Electron, Waltham, MA). A 2.8 m × 3.2 mm Ni column (Alltech Assoc., Arlington Heights, IL) was packed with 15% Carbowax 20M-TPA on 60–80 Gas Chrom P. The GLC operating conditions were: injector temperature, 200°C; He flow rate, 40 ml min^{-1}; column temperature programmed from 110 to 210, or 130 to 220°C at 4° min^{-1}. The TEA conditions were similar to those employed by Fine & Rounbehler (1975). Chromatographic peaks obtained from the samples were compared with standard NAs for precise retention time and quantitation.

Extracts containing apparent NAs were sealed in melting point capillary tubes and subjected to u.v. light at 365 nm for 1–2 h by the method of Doerr & Fiddler (1977). These samples were again subjected to GLC-TEA to determine if the photolabile NAs disappeared.

GLC mass spectrometric analysis

For confirmation of the identity of the NAs, a Varian-Aerograph Model 2700 GLC equipped with a 1.8 m × 2 mm (i.d.) glass column packed with 15% Carbowax 20M-TPA on Gas Chrom P was connected to a Varian MAT mass spectrometer (MS; Model 311A, Varian Assoc., Florham Park, NJ). The helium flow rate was 15 ml min^{-1}. The temperatures used were: detector, 200°C; injector port, 200°C; GLC-MS interface system, 180°C; and column programmed from 90 to 140°C at 4° min^{-1} for NDMA and NDEA, and from 140 to 180°C at 6° min^{-1} for NMOR. The MS was operated in the peak matching mode adjusted to a resolution of 1 in 10,000 or 12,000. The mass spectra were obtained at an ionizing voltage of 70 ev and an ion source temperature of 150°C. The mass-to-charge ratios (*m/e* of 74.04799) for NDMA and (*m/e* of 102.07930) for NDEA were determined on the bases of the *m/e* 69.99857 and *m/e* 99.99361 perfluorokerosene reference peaks, respectively, by measuring the difference in *m/e*. The *m/e* of 116.05857 for NMOR was determined on the basis of the *m/e* 106.07825 reference peak of xylene in a similar manner. The signal was recorded on both an oscilloscope and a recording oscillograph.

Some representative samples containing NAs as determined by GLC-TEA were analyzed by MS. Generally, injection of at least 5 ng μl^{-1} of NA was required for confirmation by this method.

Some of the water samples containing apparent NAs (Tables 5 and 6) were analyzed by a Hewlett–Packard Model 5992B (Hewlett–Packard, Palo Alto, CA) low resolution quadrupole GC-mass spectrometer. The column used was a 30 m × 0.5 mm glass capillary column coated with Ucon 5100; the oven temperature was programmed from 20° (held for 2 min) to 120°C at 10° min^{-1} for NDMA and from 20° (held for 2 min) to 150°C at 16° min^{-1} for NPIP and NMOR; the He flow rate was 3.5 ml min^{-1}; and the injector temperature was 150°C. NAs contained in the 1.0 ml DCM concentrated extracts were further reduced to 0.2–0.5 ml with a stream of nitrogen. The NAs were analyzed either from this solution or after peak collection from a Perkin–Elmer Model 3920 GC (Perkin–Elmer, Norwalk, CT) with cooled melting point capillary tubes. The GLC column and conditions used were the same as for the analysis of the NAs. About 5–6 collections were made; the final volume of the combined extracts was 10–20 μl. A full scan spectrum was obtained for one NMOR sample. For the others, 3–4 ions were monitored before and after the DCM concentrated extracts were photolyzed with u.v. light. The ions (*m/e*) monitored were: NDMA, 30, 42 and 74; NMOR, 30, 56, 86 and 116; and NPIP, 30, 42, 56 and 114. A 2 μl sample was injected into the GC-MS in the direct inject mode.

RESULTS AND DISCUSSION

For this investigation analyses were limited to volatile, GLC-amenable NAs.

Nitrosamines in pure adsorbents

Samples of adsorbents obtained from four manufacturers were extracted with DCM; the concentrations of apparent NAs detected are summarized in Table 1. For Ambersorb XE-340, the low levels of NDMA detected by GLC-TEA were *c.* 60% photolabile because of the dark orange-yellow color of the extract. Color or turbidity in solutions interfere with the efficiency of decomposition by photolysis as reported by Doerr & Fiddler (1977). For the remaining clear DCM activated carbon extracts, generally those reported in Table 1 containing $<0.03\ \mu g\ kg^{-1}$ NAs were 30–70% photolabile, indicating the possible presence of non-NA TEA responsive compounds. NDMA levels of 9.16 and 6.30 $\mu g\ kg^{-1}$ for Filtrasorb 400 and 300, respectively, and NDEA levels of 0.90 and 2.33 $\mu g\ kg^{-1}$ for Filtrasorb 400 and 2.82 $\mu g\ kg^{-1}$ for Filtrasorb 300 were confirmed by MS. Results for the four samples of Filtrasorb 400 indicate variable levels of NAs, probably associated with the manufacturing conditions.

Nitrosamines in tap water

The results obtained from our laboratory's tap water are shown in Table 2. In the first 8 samples of water (10–14 l.) that were passed through the Ambersorb XE-340 carbonaceous adsorbent at a flow rate of *c.* 1.2 l. h^{-1}, 0.003–0.006 $\mu g\ l^{-1}$ NDMA, 0.006–0.016 $\mu g\ l^{-1}$ NMOR and trace levels of apparent NDEA were detected. The last 10 water samples (28–42 l.) obtained at a slower flow rate of 0.39 to 0.51 l. h^{-1} yielded 0.003–0.005 $\mu g\ l^{-1}$ NDMA, 0.006–0.018 $\mu g\ l^{-1}$ NMOR and detectable levels of apparent NDEA. The source of these NAs in the tap water is not known. Several of the water samples were combined to give sufficient quantities for MS confirmation of NDMA and NMOR. Apparent NMOR in samples 15 and 16 in Table 2 were not confirmed by MS but were determined to be photolabile.

Figure 1 shows a typical TEA chromatogram (sample 17) before and after photolysis with u.v. light. For well defined samples containing confirmable levels of NAs we have found a high correlation between photolability of apparent NAs and MS con-

Table 1. Nitrosamines in commercial adsorbents

Adsorbent	Sample no.	Apparent nitrosamines ($\mu g\ kg^{-1}$) NDMA	NDEA	NMOR
Ambersorb XE-340	1	0.08	<0.01	<0.03
	2	0.09	<0.01	<0.03
Westvaco Nuchar WVW	1	Trace	<0.01	<0.03
	2	0.07	<0.01	0.09
	3	0.14	<0.01	0.11
Westvaco Nuchar WVG	1	0.14	0.09	<0.03
Filtrasorb 400	1	0.03	0.90*	<0.03
	2	0.28	0.02	0.61
	3	0.07	0.11	<0.03
	4	9.16*	2.33*	0.33
Filtrasorb 300	1	6.30*	2.82*	0.07
ICI Hydro-Darco	1	0.11	<0.01	0.16

* Confirmed by MS.

firmation (Fiddler, unpublished). Therefore, where NA levels were too small for confirmation by MS, the disappearance of a TEA responsive peak after subjection to u.v. light provided additional evidence for the presence of NAs.

Recovery studies

Recovery data on seven volatile NAs in water by Ambersorb XE-340 are summarized in Table 3. When the influent was distilled water containing added NAs, the recovery varied from 58 to 99%. Recovery of NAs added to tap water varied from 65 to 95%, except for NMOR in sample 3. The reason for the high recovery of NMOR is not known. It may have been due to the variability in the extraction of NAs or a response by the TEA to a non-NA eluting at the same time as NMOR.

Addition of amines and $NaNO_2$ to tap water prior to passage through Ambersorb XE-340

Apparent NAs found after tap water, with and without added DMA, DEA, and MOR or $NaNO_2$, was passed through the Ambersorb XE-340 column are shown in Table 4. Added 1 mg l^{-1} $NaNO_2$ in the influent (which is much higher than normally found in tap water; see Table 7) apparently had a minor effect

Table 2. Nitrosamines detected in tap water after concentration by Ambersorb XE-340

Water sample	Flow rate l h^{-1}	Total influent* (l.)	Nitrosamines ($\mu g\ l^{-1}$) NDMA	NDEA	NMOR
1	1.18	10	0.006†	0.0005	0.016†
2	1.22	14	0.005†	0.0007	0.008†
3	1.19	14	0.003‡	<0.0001	0.007‡
4	1.22	14	0.003‡	0.0007	0.006‡
5	1.18	13	0.006§	0.0005	0.015§
6	1.22	14	0.004§	0.0005	0.012§
7	1.18	13	0.005¶	<0.0001	0.011¶
8	1.22	14	0.003¶	<0.0001	0.008¶
9	0.50	32	0.003‖	0.0003	0.017‖
10	0.50	34	0.004‖	0.0003	0.018‖
11	0.51	36	0.004‖	0.0002	0.015‖
12	0.51	36	0.003‖	0.0002	0.009‖
13	0.40	38	0.004‖	0.0002	0.006‖
14	0.39	28	0.004‖	0.0003	0.007‖
15	0.40	38	0.003‖	0.0002	0.007
16	0.49	35	0.004‖	0.0001	0.012
17	0.44	42	0.005‖	0.0001	0.012‖
18	0.51	36	0.005‖	0.0001	0.012‖

* Approximate volume.
†, ‡, §, ¶ Samples with same letter were combined and confirmed by MS.
‖ Confirmed by MS.

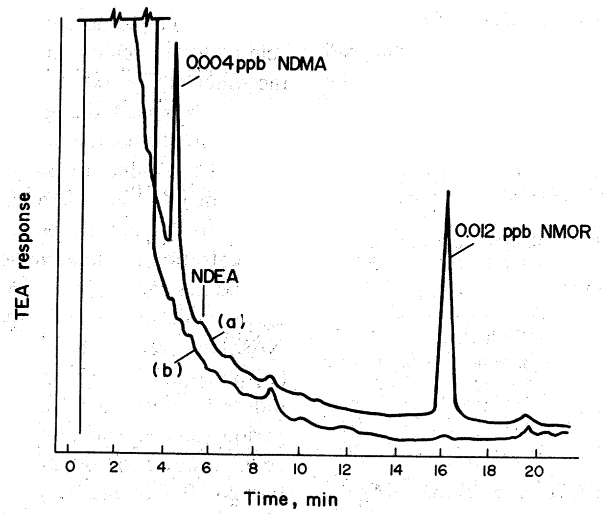

Fig. 1. GLC-TEA chromatogram (attenuation 16×) for 7.8 μl dichloromethane extract of tap water containing volatile nitrosamines. Sample 17, Table 2. (a) Before and (b) after photolysis.

on the yield of NAs, whereas added amines greatly enhanced the concentrations of the corresponding NAs. With added amines in the influent the concentrations of apparent NAs found varied in the order NMOR $\gg$ NDMA $\gg$ NDEA, which is in increasing order of the p*Ka*'s of the corresponding amines. This result was expected since rates of NA formation of secondary amines with nitrite increase with a decrease in the p*Ka*'s of the amines as reported by Mirvish (1972).

Addition of amines to tap water prior to extraction with DCM

The tap water-added amines mixture was extracted with DCM to determine if NAs were formed prior to or during passage through Ambersorb XE-340. The results shown in Table 5 indicate that added DMA, DEA and MOR reacted with component(s) of tap water to form the corresponding NAs. A low resolution full scan mass spectrum was obtained for one sample containing 9 $\mu g\ l^{-1}$ NMOR. It was identical to the spectrum of a NMOR standard. The abundance of the principal ions as a percent of the base peak abundance (*m/e* of 56 for both) for the sample and standard, respectively, was: *m/e* 30–57 and 53%; *m/e* 86–35 and 35% and *m/e* 116–34 and 37%. For a number of samples in Tables 5 and 6, a method utilizing the low resolution mass spectrometer was used in which 3–4 principal ions were monitored, and their presence before, and disappearance after, photolysis by u.v. light was considered confirmatory evidence. Thus, two samples in Table 5 were analyzed by this procedure. For the sample containing 0.864 $\mu g\ l^{-1}$ NMOR, the ions of *m/e* 116, 56 and 30, and another sample containing 0.316 $\mu g\ l^{-1}$ NDMA, the ions of *m/e* 74, 42 and 30 disappeared after photolysis with

Table 3. Recovery of added nitrosamines (NAs) by Ambersorb XE-340

Sample	Water	Flow rate ($l.\ h^{-1}$)	Total influent (l.)	Nitrosamines recovered [% or (ng)] NDMA	NMEA	NDEA	NPIP	NPYR	NMOR	NHMI
1	Distilled + NAs*	1.20	3	89†	86	88†	82	82	83†	99
	Distilled water blank	1.20	3	(4)	(<1)	(2)	(<3)	(<3)	(4)	(<3)
2	Distilled + NAs*	0.75	3	64	67	62	58	63	62	68
	Distilled water blank	0.75	3	(<1)	(<1)	(<1)	(<3)	(<3)	(<3)	(<3)
3	Tap + NAs*	0.97	30	83†	85	85†	92	93†	135†	93
	Tap water blank	0.97	30	(138)‡	(<1)	(9)	(<3)	(6)	(375)§	(<3)
4	Tap + NAs*	0.97	30	69†	76	77†	88	89†	65†	95
	Tap water blank	0.97	30	(160)‡	(<1)	(5)	(<3)	(16)	(394)§	(<3)

* 150 ng each of seven NAs: N-nitroso-dimethylamine (NDMA), -methylethylamine (NMEA), -diethylamine (NDEA), -piperidine (NPIP), -pyrrolidine (NPYR), -morpholine (NMOR) and -hexamethyleneimine (NHMI).

† % recovery determined after subtracting ng NA in water without added NAs.

‡ Confirmed by MS.

§ Combined and confirmed by MS.

Table 4. Apparent nitrosamines detected in tap water containing added amines after passage through Ambersorb XE-340

Influent*	Nitrosamine ($\mu g\,l^{-1}$) NDMA	NDEA	NMOR
10 l. tap water plus:			
None	0.0014	0.0003	0.005
1 $mg\,l^{-1}$ $NaNO_2$	0.0027	0.0005	0.006
1 $mg\,l^{-1}$ DMA, DEA, MOR†	0.09‡	0.02‡	1.3‡

* Flow rate, 11 bed v h^{-1} or 900 ml h^{-1}.
† Dimethylamine (DMA), diethylamine (DEA), morpholine (MOR); no $NaNO_2$ added.
‡ Confirmed by MS.

u.v. light. Logsdon *et al.* (1977) reported that NAs can form during the extraction of chlorinated aqueous solutions containing amines with DCM. NAs were not detected when the residual chlorine was eliminated with stoichiometric concentrations of Na_2SO_3 prior to extraction with DCM. Therefore Na_2SO_3 was added to the water in our experiments. With 10 $\mu g\,l^{-1}$ DMA, DEA and MOR added to tap water, higher levels of apparent NAs were detected when Na_2SO_3 was absent than when it was added prior to extraction with DCM. The presence of an oxidizing agent that enhanced apparent NA formation in tap water was suggested by the detection of 0.316 $\mu g\,l^{-1}$ NDMA, 0.044 $\mu g\,l^{-1}$ NDEA, and 9.0 $\mu g\,l^{-1}$ NMOR when 1 $mg\,l^{-1}$ DMA, DEA and MOR were added to tap water followed by addition of Na_2SO_3 prior to extraction with DCM. However when Na_2SO_3 was added to tap water before the amines were added, Nas levels were reduced to <0.002 $\mu g\,l^{-1}$ for NDMA and NDEA, and 0.034 $\mu g\,l^{-1}$ for NMOR. These results suggest that chlorine or some other oxidizing agent present in our laboratory's tap water may promote NA formation in the presence of secondary amines.

Addition of sulfamic acid, piperidine, and Na_2SO_3 to tap water prior to passage through Ambersorb XE-340

To determine if the NAs found in water were formed on the resin, experiments were performed with piperidine added as an amine source and sulfamic acid added to remove nitrite. Sulfamic acid added to the water at the 1000 $mg\,l^{-1}$ level lowered the pH to 2.5 and removed the nitrite within 2 min as determined by the Griess colorimetric method (Fiddler, 1977). The results are shown in Table 6. Piperidine was added to the sulfamic acid solution prior to addition to tap water (Exps 1a and 2a). Even though the concentration of sulfamic acid was much larger than the amines normally found in water, the nitrosating agent could conceivably react with amines to form NAs. However, the low levels of NPIP found in Exps (1a) and (2a), 0.0002 and 0.0004 $\mu g\,l^{-1}$, respectively, indicated that NAs were not being formed during the period when nitrite was being destroyed by sulfamic acid. Addition of 100 $\mu g\,l^{-1}$ piperidine to tap water formed 0.0926 $\mu g\,l^{-1}$ NPIP (Exp. 1), but when 100 $mg\,l^{-1}$ Na_2SO_3 was added prior to addition of the amine, NPIP formation was reduced to 0.0011 $\mu g\,l^{-1}$ (Exp. 2), indicating that the NPIP was formed in the water and not on the resin. The presence or absence of sulfamic acid did not alter the levels of NDMA and NMOR. These latter results suggested that nitrite on the resin was not a factor, since the level of these NAs were similar. Addition of 100 $\mu g\,l^{-1}$ piperidine was greater than the concentration of the normally occurring precursors for NDMA and NMOR, as indicated by the NPIP level found (0.0926 $\mu g\,l^{-1}$) compared to that of NDMA (0.0045 $\mu g\,l^{-1}$) and NMOR (0.0043 $\mu g\,l^{-1}$) in Exp. (1). Since the fate of piperidine should be similar to the amine precursors on the resin, the much lower level of NPIP compared to NDMA and NMOR (7–18 times lower) found in Exps (1a), (2), and (2a) indicates that NA formation on Ambersorb XE-340 was minor. The extremely low levels of the NAs detected for the distilled water control probably were present in the distilled water, resin, and reagents. These levels were considerably lower than the levels found in tap water; therefore, the resin and the reagents used were not the source of the NAs found in tap water.

Samples from Exps (1) and (2) were combined and then analyzed by low resolution mass spectrometry. The following ions (*m/e*) were monitored: NDMA, 30, 42 and 74; NPIP, 30, 42, 56 and 114; and NMOR, 30,

Table 5. Apparent nitrosamine formation in tap water containing added amines

Tap water plus added amines*	Added Na_2SO_3 ($mg\,l^{-1}$)	Apparent nitrosamines† ($\mu g\,l^{-1}$) NDMA	NDEA	NMOR	% Recovery, NHMI (internal std)
10 $\mu g\,l^{-1}$	None	0.070	0.108	0.864	110
10 $\mu g\,l^{-1}$	100‡	0.048	0.006	0.332	90
1 $mg\,l^{-1}$	50‡	0.316	0.044	9.0	—
1 $mg\,l^{-1}$	50§	<0.002	<0.002	0.034	96

* Dimethylamine, diethylamine and morpholine.
† In 500 ml water.
‡ Added after addition of 1 $mg\,l^{-1}$ or 10 $\mu g\,l^{-1}$ amines.
§ Added prior to addition of 1 $mg\,l^{-1}$ amines.

Table 6. Apparent nitrosamines in tap water containing piperidine, sulfamic acid, or sodium sulfite after passage through Ambersorb XE-340

Exp.	Influent* (27 l.) Water—treatment	Apparent nitrosamines ($\mu g\,l^{-1}$) NDMA	NDEA	NPIP	NMOR	% Recovery, NHMI (internal std)
	Tap water—100 $\mu g\,l^{-1}$ piperidine plus:					
1	None	0.0045	0.0003	0.0926	0.0043	92
1a	1000 $mg\,l^{-1}$ sulfamic acid	0.0043	0.0006	0.0002	0.0049	87
	Tap water—100 $\mu g\,l^{-1}$ piperidine, 100 $mg\,l^{-1}$ Na_2SO_3 plus:					
2	None	0.0135	0.0003	0.0011	0.0080	89
2a	1000 $mg\,l^{-1}$ sulfamic acid	0.0127	0.0003	0.0004	0.0077	92
	Distilled water:					
3	None	0.0003	0.0001	<0.0001	<0.0001	93
3a	100 $\mu g\,l^{-1}$ piperidine, 100 $mg\,l^{-1}$ Na_2SO_3 and 1000 $mg\,l^{-1}$ sulfamic acid	0.0007	0.0002	0.0001	<0.0001	98

* Added 90 ng (0.003 $\mu g\,l^{-1}$) NHMI.

56, 86 and 116. For NDMA the three peaks were present before photolysis; however, after treatment with u.v. light, the peaks at *m/e* 30 and 42 disappeared, but 25–33% of the 74 peak remained, indicating that at least one other compound was eluting at the same time as NDMA. All ions monitored for NPIP were strong and disappeared upon photolysis. The peaks for NMOR—four ions for samples from Exps (1) and (1a) and the *m/e* 116 and 86 ions in samples from Exps (2) and (2a)—were weak and disappeared on photolysis.

Nitrate and nitrite content of tap water

Tap water was analyzed for nitrate and nitrite concentration for a period of 1 month. The samples in Table 7 correspond to the first eight in Table 2. Levels of NO_3^- as N varied from 3–4 $mg\,l^{-1}$, whereas nitrite or nitrogen oxides levels, measured as nitrogen, were <11 $\mu g\,l^{-1}$. Lower levels of nitrite were found in the morning samples than in the afternoon samples. The nitrite values obtained by the Griess colorimetric method were generally higher than those obtained by differential pulse polarography. This, despite the fact that both methods presumably measure the same nitrosating species derived from the acidification of nitrite. The Griess method would be expected to be less accurate for low concentrations of nitrite because of optical density limitation and hence sensitivity is a function of cell light path. The two afternoon samples containing the highest nitrite levels as determined by differential pulse polarography corresponded to samples 1 and 5 on Table 2. Of the first eight samples these two also showed the highest level of NDMA (0.006 $\mu g\,l^{-1}$) and NMOR (0.015 and 0.016 $\mu g\,l^{-1}$). No pattern was evident for the remaining nitrite and NA values.

Table 7. Nitrate and nitrite content of tap water

Sample	NO_3^- ($mg\,l^{-1}$ N)	NO_2^- ($\mu g\,l^{-1}$ N) (time) AM Griess	AM DPP*	PM Griess	PM DPP
1	3	4	2	10	7
2	3	6	4	8	4
3	3	7	3	8	3
4	4	6	1	8	2
5	3	3	1	7	6
6	4	2	†	6	2
7	3	<1	<1	8	4
8	4	3	<1	9	4

* Differential pulse polarography.
† Not analyzed.

CONCLUSION

Trace levels of NAs present in tap water were accumulated by passage through Ambersorb XE-340. NAs were detected when low levels of secondary amines were added to tap water, indicating that the water possessed nitrosating ability. The experiments performed herein indicate that the nitrosamines found in tap water did not result from formation on the resin. Therefore, the trace levels of NDMA and NMOR may have resulted from the reaction of low levels of nitrite, an oxidizing agent (possibly chlorine) and amines that may be simultaneously present in tap water, or present in the water before chlorination.

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Note: Precaution should be exercised in the handling of nitrosamines since they are potential carcinogens.

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